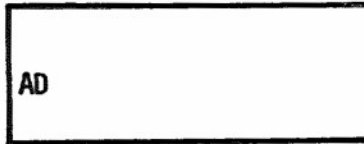LEVEL
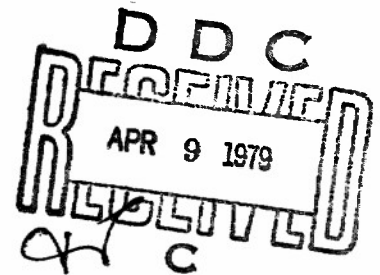
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TECHNICAL REPORT 7807

AUTOMATED NITROCELLULOSE ANALYSIS

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DECEMBER 1978

US ARMY MEDICAL RESEARCH and DEVELOPMENT COMMAND

Fort Detrick
Frederick, MD 21701

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An automated method of analysis was developed for nitrocellulose in wastewaters, with specific provision for the removal of interfering nitrite ion. The procedure, utilizing a Technicon AutoAnalyzer, involves aspiration of a stirred nitrocellulose suspension, dialysis against 9 percent saline, and hydrolysis with 5N sodium hydroxide at 70°C for 10 minutes to release nitrite ion. Sulfanilic acid is diazotized by the nitrite ion at low pH. The resulting diazonium salt is coupled with N-(1-naphthyl)ethylenediamine, and the

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20. Abstract (Cont'd)

color so produced is measured at 520 nm. The limit of detectability of nitro-cellulose is 0.4 mg/liter, well below the 1983 Best Available Technology Effluent Limitation for particulates, 10 mg/liter, which is likely to govern the discharge of nitrocellulose.

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INTRODUCTION

As a water pollutant, nitrocellulose (NC) differs from most others in that it occurs entirely as insoluble fibrous particles. Nitrocellulose is a principal ingredient of all military propellants.[1] Five Army facilities, Radford Army Ammunition Plant (RAAP), Badger Army Ammunition Plant (BAAP), Indiana Army Ammunition Plant (IAAP), Sunflower Army Ammunition Plant (SAAP) and Alabama Army Ammunition Plant (AAAP) represent by far the largest NC manufacturing capability in the U.S.A. Production at RAAP is not now at its peak level, and the other ammunition plants are currently inactive. In aggregate, these sites represent the potential for large scale water pollution by NC fines, should the manufacture of NC be accelerated. They are also repositories for settled material that can be released periodically where storms stir up the bottoms of the ponds or lakes in which the NC is contained.

Nitrocellulose, a cellulose ester of nitric acid, and more properly referred to as cellulose nitrate, is depicted in Figure 1. It is a non-volatile, fibrous, white, solid polymer. Production-grade NC is rather dense (sp gr 1.65). Although insoluble in water, NC dissolves in acetone; certain forms are also soluble in 2:1 ether:alcohol.[2] As shown in Figure 1, NC contains three nitrate ester groups per glucose moiety, in which case the theoretical nitrogen content is 14.14 percent. In reality, since the degree of nitration is not always complete, nitrogen contents as low as 6.76 percent have been reported, but such low values are not found in military grade NC.[3] A generalized empirical formula for NC with varying nitrate ester contents would be $C_6H_7O_2(OH)_{3-x}(ONO_2)_x$; no product representing a homogeneous mono- or dinitrate ester, i.e., x = 1 or 2, has been obtained.[3] In boiling tub pit water NC fines, 97 percent of the particles are less than 20 microns in size, and about 30 percent less than 1 micron.[1] Most of the NC in a suspension can be removed from water by filtration through a 0.45-micron filter, and high-speed centrifugation can be used to remove the majority of that which passes through such a filter.
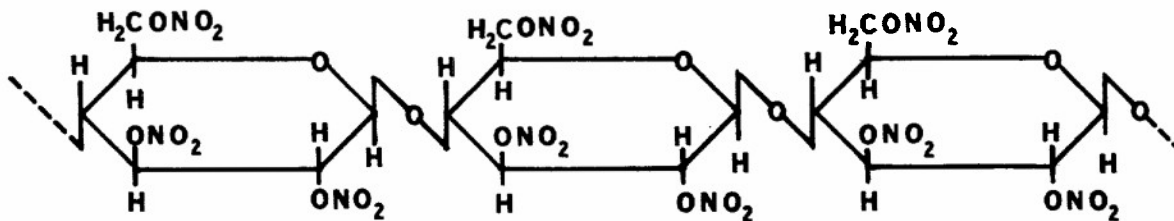

Figure 1. Partial Structure of Fully Nitrated Nitrocellulose in Which Each Glucose Moiety has Three Nitrate Ester Groups Attached.

Nitrocellulose is essentially inert and long-lasting under most environmental conditions.[1] It has apparently never been considered a particularly harmful pollutant for either water or sediment. Its remarkably low toxicity to mammals and aquatic organisms has recently been established.[4] Thus, the limiting factor for nitrocellulose concentrations in discharged waters should continue to be the water quality criterion regulating total suspended solids (TSS) in wastewater discharges.[4] This value (Best Available Technology Effluent Limitations, Explosive Manufacturing) will be 10 ppm, as of 1 July 1983.[5] At present, the only analytical method in use for NC in wastewaters consists of collecting suspended solids on filters and weighing them; it fails to distinguish between nitrocellulose and such inert materials as clay particles. A facile automated method for determining the NC content of discharge waters, and perhaps of receiving waters, would be useful to the US Army Environmental Hygiene Agency, the US Army Materiel Development and Readiness Command, and munitions plant operators for surveying and monitoring nitrocellulose particulate discharges from Army ammunition plants. In those cases where particulate discharge levels were excessive, the analytical method would aid in identifying the cause. In addition, it would alert manufacturers to malfunctions in the removal of nitrocellulose fines from wastewater streams.

Historically, the analytical methodology for NC has been oriented towards propellant quality control, i.e., towards determining the degree of nitration of NC or the content of NC in a propellant mixture. Some of the more noteworthy methods are the following: The ferrous-titanous titration method of Pierson and Julian;[6] nitrate ester determinations cited by Verschragen[7] that use ferrous sulfate titration or evolution of nitric oxide or reduction to ammonia with Devarda's alloy (10:9:1 mixture of copper, aluminum and zinc); a new titrimetric method involving trans-nitration of salicylic acid, followed by addition of titanous ion and back-titration of excess titanous ion with ferric ammonium sulfate, as described by Stalcup and Williams in 1955;[8] a chromous chloride-ferric ammonium sulfate microdetermination described by Selig in 1961;[9] and determination of nitrogen by the Dumas method.[10] All these methods are time-consuming, tedious, primarily titrimetric in nature (except the last), and lacking in the sensitivity required for trace amounts of nitrocellulose in wastewaters. Thus they do not have the potential for automation.

Two methods for nitrate esters that depend on the formation of nitrite ion were recently found in Army ammunition plant files. The first of these was used at BAAP for determining nitroglycerin collected from the air in impingers,[1] through zinc dust reduction of the nitrato group; although the procedure's applicability to quantitative NC determination is implied, there is some doubt as to the feasibility of this ostensibly solid-solid reaction. The second method, furnished by Dr. William Bolleter from Hercules Corporation files at RAAP,[1] depends on hydroxide ion attack on NC in acetone solution to produce nitrite ion, as expected on the basis of the literature; released nitrite ion is then determined.

Since this method requires the use of acetone, which attacks the plastic tubing that must be used in the peristaltic pumps of an automated system, it cannot be directly automated. Both of these inherently sensitive procedures for nitrate esters depend on the formation of nitrite ion (along with nitrate ion) and the use of the latter to diazotize one aromatic amine, which is then coupled into another aromatic amine; this is the Griess method. It should be noted, at this point, that the formation of nitrite ion is somewhat unexpected, considering the general behavior of organic esters of inorganic acids; nitrate ion formation would be normal in such a hydrolysis reaction. Both nitrate and nitrite are formed, but a particular ratio of these to one another can be maintained only by scrupulous reproduction of conditions. Alternatively, the nitrate ion can be reduced to nitrite in a separate step, thereby potentially increasing analytical sensitivity somewhat, as well as avoiding variability due to inconstancy of the nitrite:nitrate ratio.

It remained to be seen if the ratio of surface to weight for a typical military nitrocellulose dispersion in water would be great enough to permit reasonably rapid formation of nitrite ion by hydroxide attack, i.e., in a heterogeneous reaction, under appropriate conditions.

OBJECTIVE

The objective of this investigation was to develop first a manual and then an automated analytical method for waterborne nitrocellulose particulates in the low ppm range for the analysis of wastewaters from Army ammunition plants.

EXPERIMENTAL APPROACH

The overall principles of the analytical method were first developed with manual manipulations, then converted to an automated system. The reasons for choosing the particular aromatic amine reagents used here will be discussed later on.

A. For the manual system, the following steps were involved (where R' can be H or a carbon-containing group):

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2. $NO_2^- + H^+ + H_3\overset{+}{N}-$⬡$-SO_3^- \longrightarrow$

$N\equiv\overset{+}{N}-$⬡$-SO_3^- + 2\ H_2O$

3. $H_2N-CH_2-CH_2-\overset{H}{\underset{|}{N}}-$⬡⬡ (NED) $+ N\equiv\overset{+}{N}-$⬡$-SO_3^-$

$H^+ + H_2N-CH_2CH_2-\overset{H}{\underset{|}{N}}-$⬡⬡$-N=N-$⬡$-SO_3^-$
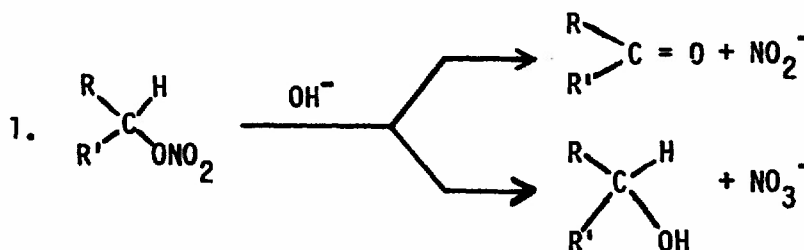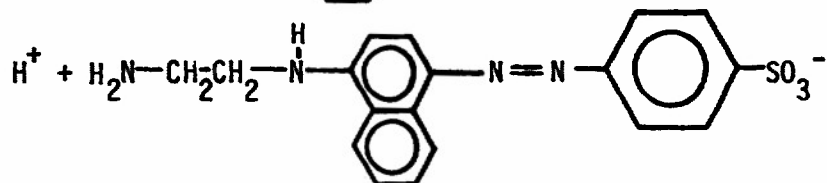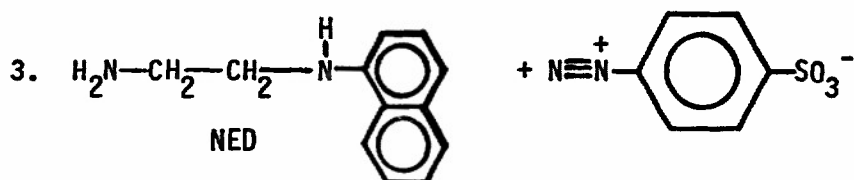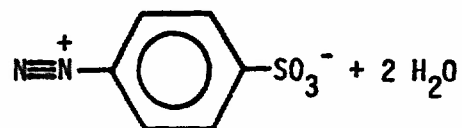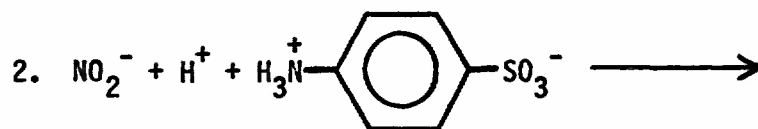
Red Dye

B. In the automated approach, two important additional features were introduced, namely steps 1 and 3 in the following scheme:

1. Dialysis of NC suspension to remove NO_2^- and NO_3^-.

2. $\underset{R'}{\overset{R}{\diagdown}}\underset{ONO_2}{\overset{H}{C}}\ \xrightarrow{OH^-}$
$\underset{R'}{\overset{R}{\diagup}}C=O + NO_2^-$
$\underset{R'}{\overset{R}{\diagdown}}\underset{OH}{\overset{H}{C}} + NO_3^-$

3. $NO_3^- \xrightarrow[NH_4^+Cl^-]{Cd} NO_2^-$ (When NO_3^- is included in analysis)

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4. $NO_2^- + H^+ + H_3\overset{+}{N}$ —⬡— SO_3^- ⟶

$\overset{+}{N}\!\equiv\!N$ —⬡— $SO_3^- + 2\ H_2O$

5. $H_2N\!-\!CH_2\!-\!CH_2\!-\!\overset{H}{N}$—⬢⬢ (NED) $+\ N\!\equiv\!\overset{+}{N}$ —⬡— SO_3^- ⟶

NED

$H^+ + H_2N\!-\!CH_2\!-\!CH_2\!-\!\overset{H}{N}$—⬢⬢—$N\!=\!N$—⬡—$SO_3^-$
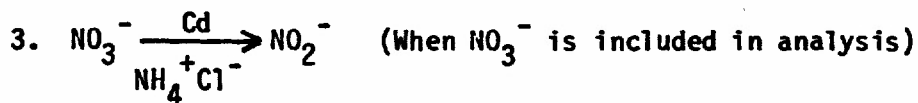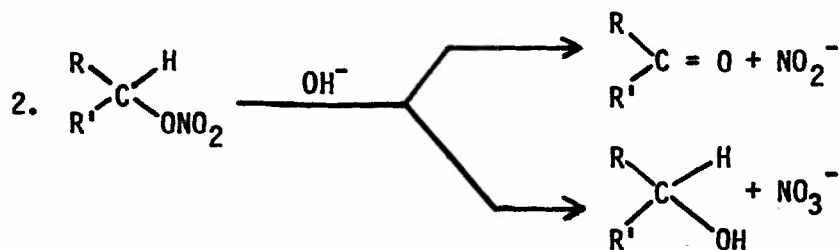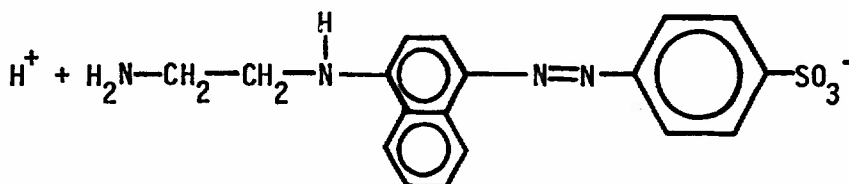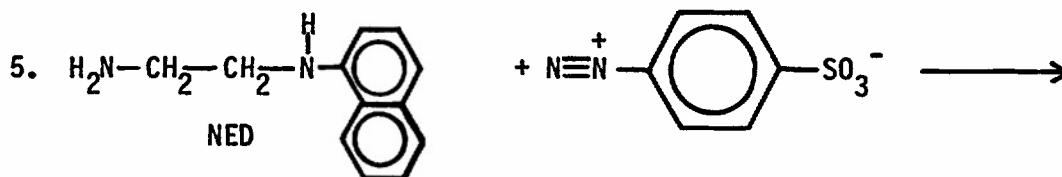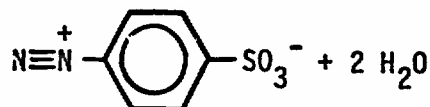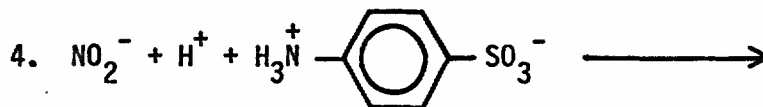
Red Dye

REAGENTS, EQUIPMENT AND METHODS

Reagents

Nitrite-free Water. Distilled water was passed through a mixed-bed deionizing column, followed by an activated carbon column. The water had to be free of nitrite ion and manganese.

5N Sodium Hydroxide. To a 1-liter volumetric flask was added 500 ml of chilled nitrite-free water, and 200 g of ACS grade NaOH pellets were then added; after all the pellets were dissolved, the solution was diluted to the mark and stored in a plastic screw-top bottle.

0.034M Sulfanilic Acid. Six grams of sulfanilic acid were added to 500 ml of hot (80°C) nitrite-free distilled water with mixing, and to this add 200 ml of concentrated HCl; the solution was cooled to room temperature after all of the sulfanilic acid was in solution and diluted to 1 liter.

N-(1-Naphthyl)ethylenediamine (NED). To a 250-ml red or brown glass flask 300 mg of NED were added, followed by 99 ml of NO_2^--free water and 1 ml of concentrated HCl. This reagent had to be made daily, kept cold and protected from light.

1% Ammonium Chloride. Ten grams of ammonium chloride were dissolved in 1 liter of 4.5 N hydrochloric acid.

Wetting Agent for Addition to Samples for Automated Analysis. A solution of 0.1 percent Brij-35 (Technicon Chemicals and Supplies) in 9 percent saline was used as a wetting agent to assist in the smooth passage of the NC particles through the automated analysis system.

Dialysis Countersolution. A 9 percent sodium chloride solution was employed as the countersolution in the Technicon AutoAnalyzer dialyzer units.

Standard Nitrite Solutions

1. Stock Solution (250 mg/l as N): Sodium nitrite (1.232 g) was dissolved in double-distilled deionized nitrite-free water and diluted to 1 liter, with addition of 1 ml of chloroform as a preservative. The stock solution was standardized by the method found in "Standard Methods for the Examination of Water and Wastewater."[11] This solution was kept refrigerated.

2. Intermediate Nitrite Solution (10 mg/l as N): Four milliliters of the stock solution were diluted to 100 ml. This solution was made daily.

3. Working Nitrite Solutions: Aliquots (2, 4, 6, 8, and 10 ml) of the intermediate solution were diluted to 100 ml. These dilutions yielded concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 mg/l NO_2^- as N, respectively. The solutions were prepared daily.

Standard Nitrate Solutions

1. Stock Nitrate Solution (250 mg/l as N): Potassium nitrate (1.804 g) was dissolved in double-distilled deionized nitrate- and nitrite-free water.

2. Intermediate Nitrate Solution (20 mg/l as N): Eight milliliters of the stock solution were diluted to 100 ml.

3. Working Nitrate Solutions: Aliquots (1, 2, 4, 6, 8, and 10 ml) of the intermediate solution were diluted to 100 ml. These dilutions yielded concentrations of 0.2, 0.4, 0.8, 1.2, 1.6, and 2.0 mg/l NO_3 as N, respectively. The solutions, stored in a refrigerator and protected from light were prepared daily.

Standard Nitrocellulose Suspensions

1. Primary NC Suspension: The nitrogen content of production grade NC (Badger Army Ammunition Plant) was determined through analysis in a Perkin-Elmer Elemental 240 Analyzer. Enough of the dried material was suspended in nitrite-free water to yield a 1 g/l suspension; this was stored, under refrigeration, in a brown glass bottle.

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2. Intermediate NC Suspension: Enough of the NC suspended in the primary suspension was removed by means of a large-bore pipet to yield, on suitable solution, a concentration of 70 mg/l of NC. To insure that the full particle range of the NC was collected for the intermediate suspension, the primary suspension was continuously and vigorously stirred as sampling is carried out.

3. Working NC Suspensions: Serial dilutions were made of the vigorously stirred intermediate suspension by taking 2, 4, 6, 8, and 10 ml aliquots and diluting them to 100 ml. The concentrations of the working standards were calculated from the nitrogen content found in the production sample. The suspensions were made daily and stored refrigerated and protected from light.

Cadmium Reductor. A 35-cm/2.0 mm ID glass tube (Technicon Model P/N 189-0000) was filled with cadmium powder (Technicon Cat. No. P/N T11-5063) and activated with 2 percent (w/v) aqueous copper sulfate solution.

Glyceryl Trinitrate Solution. A tablet of Dow Chemical Co. glyceryl trinitrate (10 percent "nitroglycerine"/90 percent lactose) was dissolved in a small amount of absolute ethanol, filtered, and diluted with water to give a solution containing 6 mg/liter of nitroglycerine. This stock solution was mixed with NC suspensions to give various concentrations of each component.

Partially Treated Domestic Wastewater. Six unfiltered samples were obtained (and used the next day) as follows:

1. Joppatown, MD, pre-chlorination, old system.
2. Joppatown, MD, pre-chlorination, new system.
3. Joppatown, MD, post-chlorination, combined old and new systems.
4. Edgewood Area, Aberdeen Proving Ground, MD, before trickling filter.
5. Edgewood Area, Aberdeen Proving Ground, MD, pre-chlorination.
6. Edgewood Area, Aberdeen Proving Ground, MD, post-chlorination.

Equipment

Elemental Analyzer. Perkin-Elmer Elemental 240 Analyzer.

Colorimeter. A Bausch and Lomb Spectronic 700 colorimeter with a 520 nm filter was used for the manual analytical procedure (readings in optical density units, ODU). The external dimensions of the test tubes used as cells were 13 X 100 mm, so that the tubes had a 10-mm light path.

Automated Analytical Equipment. For the automated procedure, a Technicon AutoAnalyzer II with various modules (including AutoAnalyzer I or II dialysis modules) were assembled as shown in Figures 2a and 2b and run at the rate of 20 samples per hour, plus 20 solvent blanks (alternately). A

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Figure 2a. Technicon AutoAnalyzer Assembly for Nitrocellulose Analysis: Sampling and Dialysis Modules as Used in the Finally Adopted Configuration.
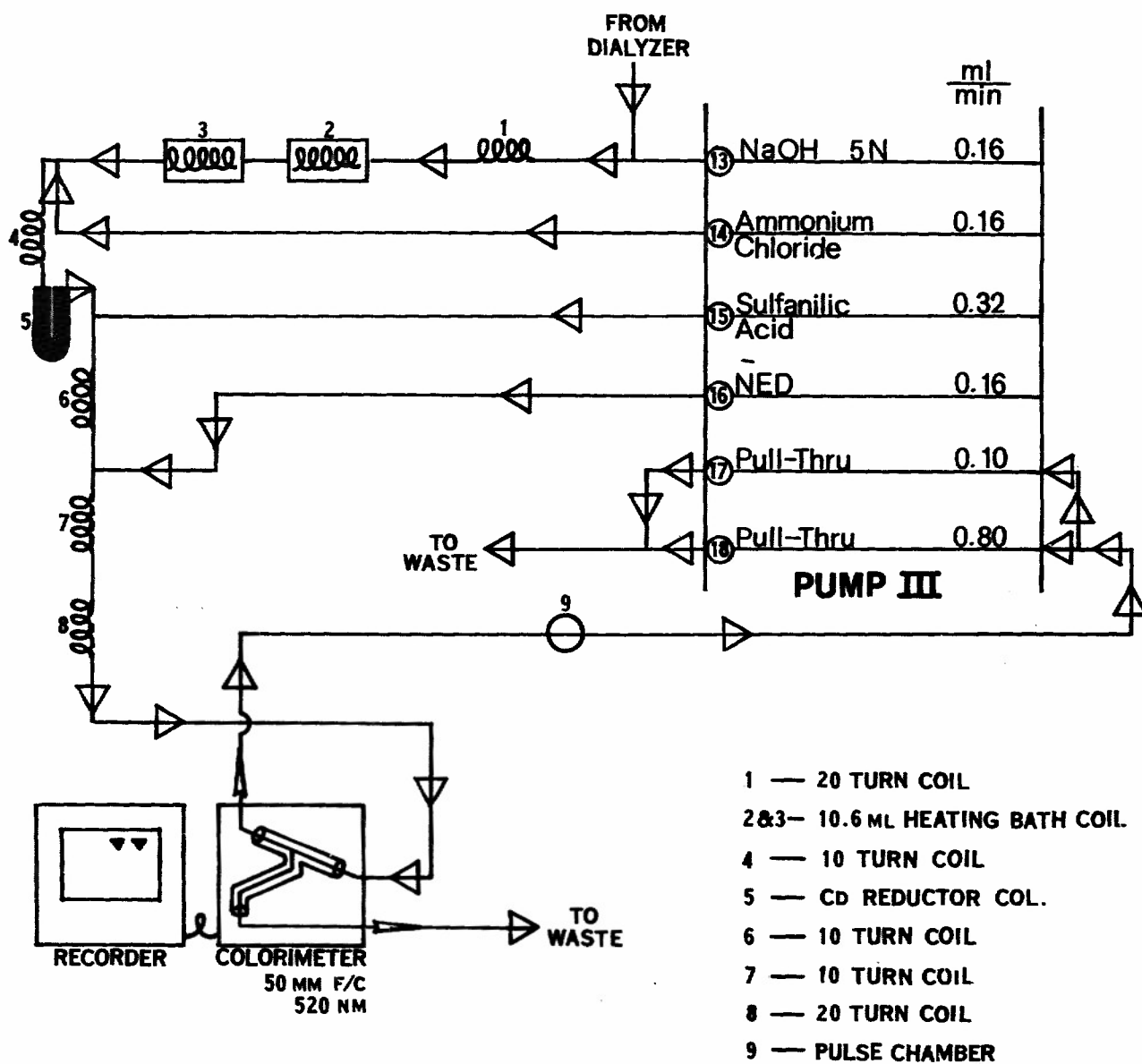
Figure 2b. Technicon AutoAnalyzer Assembly for Nitrocellulose Analysis: Sampling and Dialysis Modules as Used in the Finally Adopted Configuration.

sample:wash ratio of 6:1 was used throughout. In Figure 3, standard and countercurrent arrangements of the dialyzers are contrasted. The Technicon catalog numbers (Technicon Industrial Systems) of the modules are as follows:

Modules for Nitrite Analysis

Modules	Technicon Part Numbers
Sampler IV	171-A017-03
Pump III	133-A000-05
Type A Research Cartridge	189-A001-01
Single Channel Colorimeter	199-A001-05
Single Pen Recorder*	011-A115-01
Digital Printer (Optional)*	170-A050-02

*Colorimeter readings are in terms of peak height, not peak area.

Modules for Evaluation of Nitrite Removal by Dialysis

Modules	Technicon Part Numbers
All modules used for nitrite analysis	-
AAII 3" (7.5-cm) Dialyzer	Upper Plate P/N 177-B076-01 Lower Plate P/N 177-B006-01 Membrane* P/N 170-0406-02
Up to 3 AAII 6" (15-cm) Dialyzers	Upper Plate P/N 177-B007-01 Lower Plate P/N 177-B008-01 Membrane* P/N 170-0406-02
Up to 4 AAI Two-Plate Dialyzers	Plate** 105-A000-01 Membrane* P/N 105-0010-F01

 * Membranes were Type C cellulose with 4-6 nm pore size and sheet thickness 0.127 mm.
** Each AAI Dialyzer Plate (top or bottom) has a continuous grooved serpentine channel 220 cm long. The grooves in the top and bottom plates match, with the membrane separating them.

Modules for Nitrate/Nitrite Analysis

Modules	Technicon Part Numbers
All modules used for nitrite analysis	-
Reductor tube (filled as described above)	P/N 189-0000
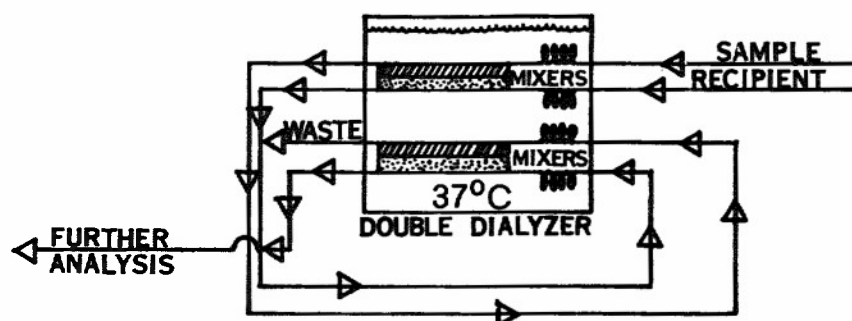
TRADITIONAL AAI DIALYSIS
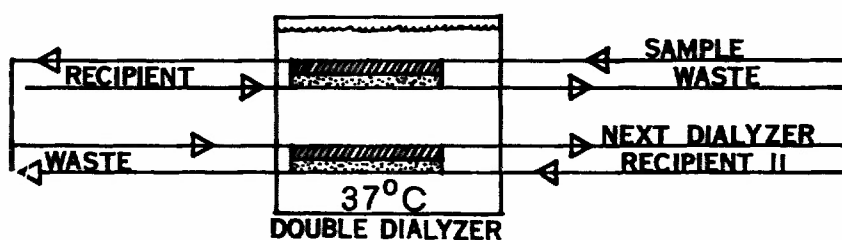
COUNTER-CURRENT DIALYSIS

Figure 3. Arrangements of Technicon AutoAnalyzer I Dialyzer Flow Connections for Traditional and Counter-Current Dialyses.

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Modules for Nitrocellulose Analysis (Nitrite Method)

Modules	Technicon Part Numbers
All modules used for nitrite analysis 4 AAI Two-plate Dialyzers (in series)	- Plates 105-A000-01 Membrane P/N 105-0010-P01

Modules for Nitrocellulose Analysis (Nitrate/Nitrite Method)

Modules	Technicon Part Numbers
All modules used for nitrate/nitrite analysis 4 AAI Two-plate Dialyzers (in series)	- Plates 105-A000-01 Membrane P/N 105-0010-A01

The colorimeter was set at 520 nm with zero damping. The Standard Calibration Potentiometer was set at 105 for earlier experiments, later at 060.

Manual Analytical Procedure

Standard Preparation. Upon receipt of the sample, which is covered with water for shipment, the NC is resuspended in the supernatant water. The NC is isolated by filtration of a 10-ml aliquot of this mixture on a 0.45-micron filter; the material is resuspended (in distilled water) and isolated three additional times. Finally, the washed NC is removed from the filter pad and resuspended in 10 ml of nitrite-free water. [Note: Whenever an aliquot is taken from an NC suspension, the suspension must be continuously agitated.]

Analysis: To 2 ml of sample (either a nitrite solution or an NC suspension) add 1 ml of 5N sodium hydroxide reagent, mix, heat to 70°C for 10 minutes, and then cool to room temperature. Add 4 ml of 0.03 M sulfanilic acid, mix, and let stand for 2 to 10 min of reaction time. Then add 1 ml of NED reagent and allow reaction to continue for at least 4 minutes. Read the red color produced within 6 hours at 520 nm. Blank determinations are handled in like manner, except that nitrite-free water is used in place of the sample.

Automated Analytical Procedure

Standard Preparation. See above.

Analysis. An NC suspension to be analyzed is continuously agitated; a portion of this suspension is aspirated from a sample cup and mixed with wetting agent solution. The mixture enters the dialysis unit where dialyzable salts, in particular nitrites and nitrates (which could interfere with the analysis), are removed; at the same time, the volume

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of the suspension decreases somewhat. After the last dialyzer, the sample stream is mixed with 5 N sodium hydroxide reagent and heated to 70°C in two 10.6-ml coils, for about 20 min. The coil effluent, containing degraded NC, nitrite ion and nitrate ion is mixed with ammonium chloride, which lowers the pH of the basic hydrolysis solution to about 8. The flow stream then enters the cadmium reductor, where the nitrate ion is reduced to nitrite. (The reductor has no effect on other constituents of the mixture.) Sulfanilic acid and NED are added in sequence. The resulting red color is allowed to develop in the last 20-turn coil. This color is read in a 50-mm flow-through cell at a wavelength of 520 nm. This procedure applies to the automated nitrate/nitrite analysis of NC. Deletion of one or more steps provides descriptions for automated analyses reported below.

RESULTS

Elemental Analysis of Nitrocellulose

Analysis of a washed and dried sample of nitrocellulose on the elemental analyzer indicated a nitrogen content of 12.6 percent, as opposed to the theoretical value of 14.14 percent. In later comparisons of actual to theoretical yields of nitrite or nitrate/nitrite, the 12.6 percent value was used for calculations.

Manual Method

Nitrite Analysis. Results are shown in Table 1 and plotted in Figure 4. The plots were linear; four separate runs gave a sensitivity of 1.913×10^{-3} mg/l (as N) per ODU, with a standard deviation of 1.267×10^{4} mg/l (as N) per ODU.

TABLE 1. DATA FOR MANUAL GRIESS NITRITE TEST

Nitrite Ion Concentration in mg/l (as N)	Net Optical Density Units (ODU)			
	29 Jan 74	11 Mar 74	11 Mar 74	11 Mar 74
Blank (gross)	26	14	10	9
0.1	44	--	--	--
0.20	109	--	--	--
0.25	--	117	135	128
0.30	178	--	--	--
0.40	229	--	--	--
0.50	292	245	248	254
0.60	337	--	--	--
0.75	--	357	402	388
0.80	457	--	--	--
1.00	--	465	548	542

CALIBRATION FACTORS
(MG/1/ODU) = F

1 ———— F = 1.91
2 ———— F = 1.73
3 ·········· F = 2.17
4 — — — F = 1.86
5 ——————— F = 1.91
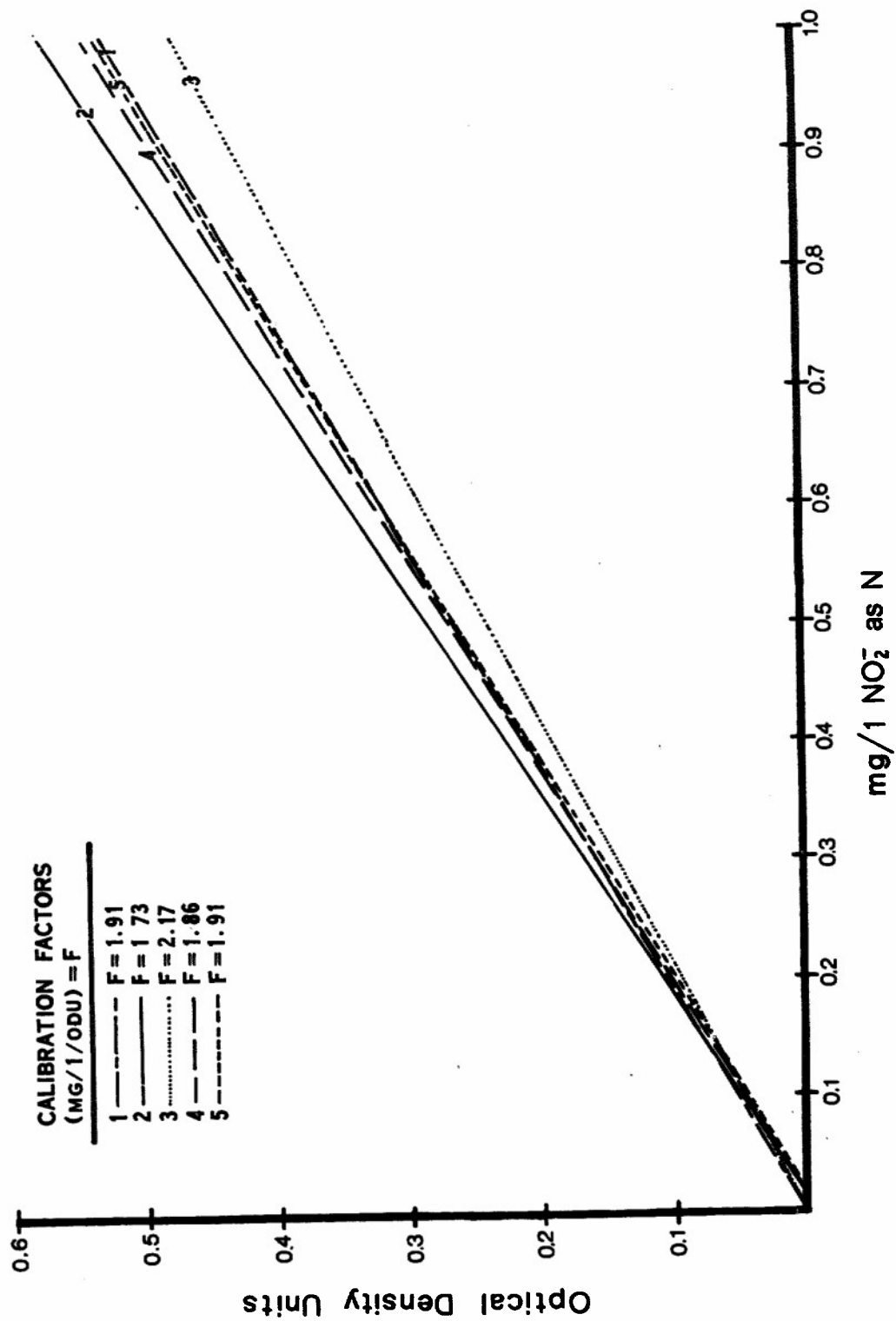
Figure 4. Plots for Manual Nitrite Analyses.

mg/1 NO$_2^-$ as N

Optical Density Units

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Nitrocellulose Analysis. Results are shown in Table 2. Based on the dried weight of a sample of NC that was resuspended and analyzed, 67.3 percent of the stoichiometric yield of nitrite ion (assuming no nitrate formation) was obtained. Ten identical samples of NC suspension, 0.5 mg/l (as N), were analyzed to establish the reproducibility of the method. The results (Table 3) indicated a mean of 260 ODU, standard deviation = 15 ODU. Under the experimental conditions less than 50 percent of the nitrate ester groups were hydrolyzed. Based on these results, the minimum detectable concentration of NC by the manual method would be about 1 mg/l (as NC).

TABLE 2. DATA FOR MANUAL GRIESS TEST APPLIED TO HYDROLYZED NITROCELLULOSE

Nitrocellulose Concentration, mg/l	Theoretical Nitrite Concentration, mg/l (as N)	Found Nitrite Concentration, mg/l (as N)	Yield of Nitrite, %
1.4	0.18	0.11	62.4
2.6	0.33	0.23	70.2
5.3	0.67	0.46	68.9
7.9	1.00	0.69	69.3
10.6	1.34	0.88	65.9
		Average	67.3

TABLE 3. REPRODUCIBILITY OF ANALYSIS
FOR 0.5 mg/l NITROCELLULOSE

Sample No.	Optical Density, ODU
1	284
2	268
3	260
4	260
5	252
6	252
7	244
8	284
9	260
10	237

Automated Method

Nitrite Analysis. For this determination, the dialyzer units and the cadmium reductor (steps 1 and 3) were bypassed. The minimum visible response for a series of standards was 0.01 mg/1 (as N) of nitrite ion at a pen deflection of 2.5 units above the strip chart recorder baseline (Fig. 5). This is considerably above the noise level of the instrument. The standards were run through at a rate of 40 samples per hour with a sample to wash ratio of 2:1, and a blank between each standard and the next. The heating time of 10 min at 70°C was adequate for complete reaction. The data of Figure 5 were plotted in Figure 6, plot 1; and those of a similar experiment run 4 hours later were plotted in Figure 6, plot 2. These two plots gave calibration factors of 5.26×10^{-3} and 5.17×10^{-3} mg/1 per net chart unit, respectively.

Nitrite Removal (in Absence of NC) by Various Dialyzer Combinations. Since a nitrocellulose-containing wastewater stream will quite likely contain nitrite and nitrate ions, these ions (or at least nitrite ions) must be removed from an analyte sample before the nitrate ester groups are cleaved with base. They could be removed, of course, by isolating the particulates on a filter, washing them, and recovering them for subsequent analysis; but the time required for such a series of manual operations would offset the advantages of an otherwise automated system. For this reason dialysis was investigated.

The efficiency of dialysis was found to depend on three principal factors: The distance travelled by the analyte stream while in contact with the dialysis membrane; the initial concentration of sodium chloride in the recipient stream (countersolution); and the relative directions of flow of sample stream and recipient stream. The maximum available distance obtained with three 6" AutoAnalyzer II units in series, with a concurrent 0.9 percent NaCl solution recipient stream, and hence the efficiency of nitrite removal, was less than that of a single AutoAnalyzer I unit (i.e., half a dual unit) as shown by Table 4. Thus, only Auto-Analyzer I units were utilized in the studies that follow. The efficiencies of concurrent distilled water, 0.9 percent sodium chloride and 9 percent sodium chloride solutions in a single dialyzer unit (input 1 mg/1 $NaNO_2$ as N) were 37 percent, 41 percent and 52 percent, respectively. The latter performance was increased to 73 percent by causing the recipient stream to flow countercurrent to the sample stream. Thus, this flow reversal (with introduction of fresh 9 percent NaCl countersolution at each unit) should theoretically increase the efficiency of four in-series dialysis units from 95 percent to 99.5 percent. In fact, for most concentrations, the countercurrent system gave the efficiencies predicted by the formula: Percent Efficiency = $100 (1.00-(1.00-0.73)^n)$, where n is the number of units. Thus, the predicted efficiency values were 73 percent, 92.7 percent, 98.0 percent and 99.5 percent for one, two, three and four units; the actual values are shown in Table 5. Each dialysis unit adds an increment of 12 minutes to the analysis time.

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Automated Method

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18

Figure 5. Strip Chart Records of Automated Nitrite Analyses, Showing Minimum Detectable Level.
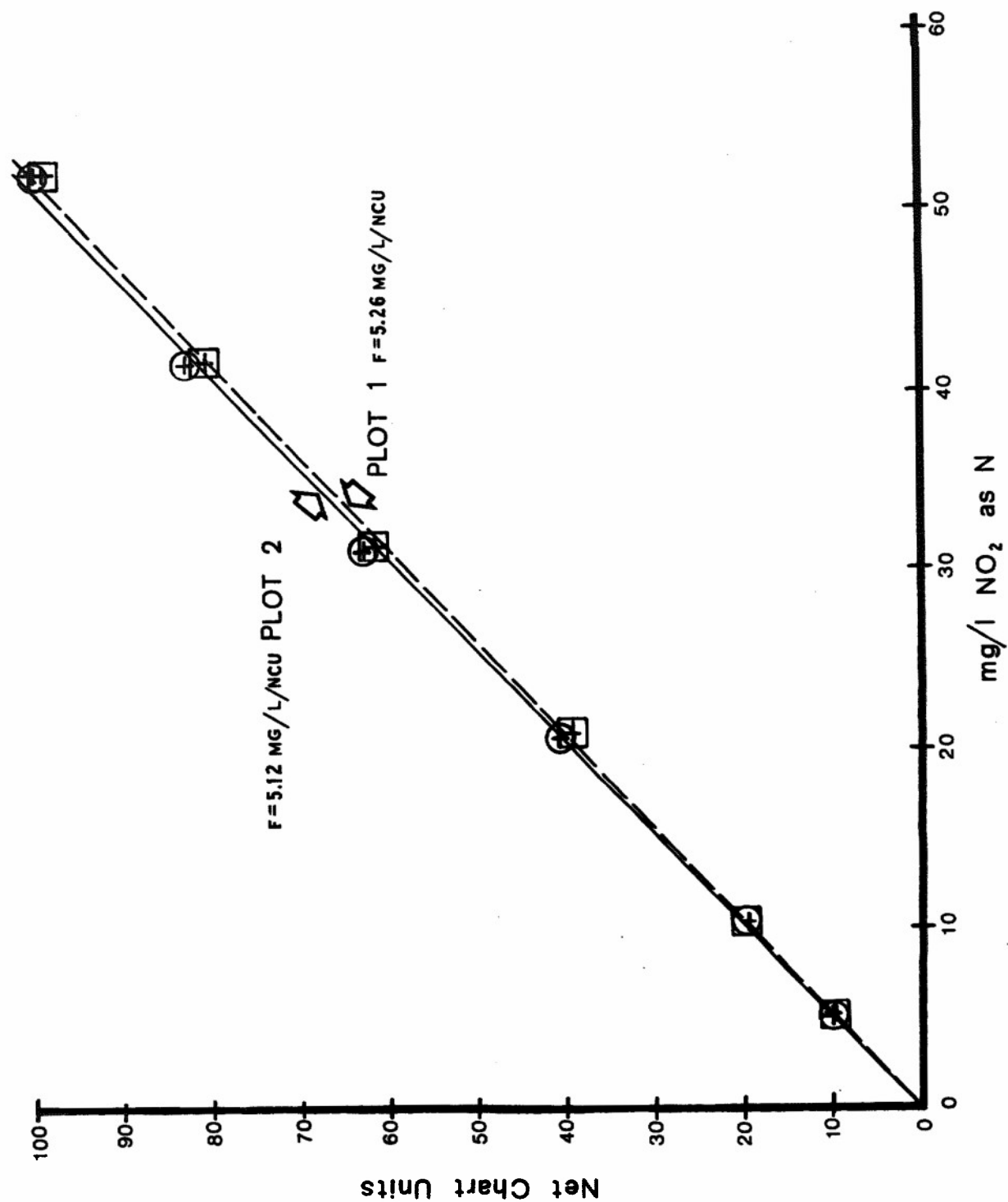
Figure 6. Data Plots for Automated Nitrite Analyses.

20

TABLE 4. PERFORMANCE OF VARIOUS DIALYZER UNITS IN THE REMOVAL OF NITRITE ION (1 mg/1 AS N, CONCURRENT WITH 0.9 PERCENT NaCl RECIPIENT STREAM)

Dialyzer Units	Removal Efficiency, %
AA II, 7.5-cm	7
AA II, 15-cm	10
AA II, Double 15-cm (30-cm)	16
AA II, Triple 15-cm (45-cm)	21
AA I, Single Unit, 220-cm	41

TABLE 5. DIALYZER EFFICIENCY OF AUTOANALYZER I UNITS IN SERIES (WITH FRESH 9 PERCENT NaCl COUNTERCURRENT RECIPIENT STREAM INTRODUCED AT EACH DIALYZER UNIT)

Nitrite Solution Input Concentration, mg/1 (as N)	Number of Dialyzer Units in Series							
	1		2		3		4	
	Output Conc., mg/1	Eff., %	Output Conc., mg/1	Eff., %	Output Conc., mg/1	Eff., %	Output Conc., mg/1	Eff., %
0.1	0.03	70.0	a	b	a	b	a	b
0.2	0.05	75.0	a	b	a	b	a	b
0.4	0.11	72.5	a	b	a	b	a	b
0.6	0.16	73.3	a	b	a	b	a	b
0.8	0.21	73.8	a	b	a	b	a	b
1.0	0.25	75.0	0.07	93.0	0.02	98.0	0.01	99.0
2.0	0.58	71.0	0.15	92.5	0.05	97.5	0.02	99.0
4.0	c	b	0.28	93.0	0.09	97.8	0.04	99.0
6.0	c	b	0.44	92.7	0.14	97.7	0.06	99.0
8.0	c	b	0.59	92.6	0.19	97.6	0.08	99.0
10.0	c	b	c	b	0.23	97.7	0.09	99.1
15.0	c	b	c	b	0.37	97.5	0.14	99.1
20.0	c	b	c	b	0.47	97.6	0.18	99.1
25.0	c	b	c	b	0.58	97.7	0.21	99.2
Mean % Efficiency		72.9		92.8		97.7		99.1
Standard Deviation for Efficiency		1.9		0.2		0.2		0.1

a. Too low to measure.
b. Not calculable.
c. Too high to measure.

21

TABLE 4. PERFORMANCE OF VARIOUS DIALYZER UNITS IN THE REMOVAL
OF NITRITE ION (1 mg/1 AS N, CONCURRENT WITH 0.9 PERCENT NaCl
RECIPIENT STREAM)

Dialyzer Units	Removal Efficiency, %
AA II, 7.5-cm	7
AA II, 15-cm	10
AA II, Double 15-cm (30-cm)	16
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(WITH FRESH 9 PERCENT NaCl COUNTERCURRENT RECIPIENT STREAM
INTRODUCED AT EACH DIALYZER UNIT)

Nitrite Solution Input Concentration, mg/1 (as N)	Number of Dialyzer Units in Series							
	1		2		3		4	
	Output Conc., mg/1	Eff., %	Output Conc., mg/1	Eff., %	Output Conc., mg/1	Eff., %	Output Conc., mg/1	Eff., %
0.1	0.03	70.0	a	b	a	b	a	b
0.2	0.05	75.0	a	b	a	b	a	b
0.4	0.11	72.5	a	b	a	b	a	b
0.6	0.16	73.3	a	b	a	b	a	b
0.8	0.21	73.8	a	b	a	b	a	b
1.0	0.25	75.0	0.07	93.0	0.02	98.0	0.01	99.0
2.0	0.58	71.0	0.15	92.5	0.05	97.5	0.02	99.0
4.0	c	b	0.28	93.0	0.09	97.8	0.04	99.0
6.0	c	b	0.44	92.7	0.14	97.7	0.06	99.0
8.0	c	b	0.59	92.6	0.19	97.6	0.08	99.0
10.0	c	b	c	b	0.23	97.7	0.09	99.1
15.0	c	b	c	b	0.37	97.5	0.14	99.1
20.0	c	b	c	b	0.47	97.6	0.18	99.1
25.0	c	b	c	b	0.58	97.7	0.21	99.2
Mean % Efficiency		72.9		92.8		97.7		99.1
Standard Deviation for Efficiency		1.9		0.2		0.2		0.1

a. Too low to measure.
b. Not calculable.
c. Too high to measure.

21

Nitrate Analysis. For this determination, the dialyzer units (step 1) were bypassed. The system used is diagrammed in Figure 7. The nearly linear results (Fig. 8) indicated a detectability of 0.05 mg/l of NO_3^- as N and a sensitivity of 2.1×10^{-3} mg/l of NO_3^- as N per net chart unit. [Note: It is known that the cadmium reductor does not reduce nitrite ion.]

Analysis of Nitrocellulose through Determination of Nitrite Ion Concentration Produced by Basic Hydrolysis. The cadmium reductor (step 3) was bypassed for this determination; two dual AutoAnalyzer I dialyzer units were employed, although not actually required since no nitrite ion was present. The raw data are presented in Table 6 and a summary of these data in Table 7. These results show a sensitivity of 0.02554 ± 0.00614 mg/l as N per net chart unit. Based on a nitrate nitrogen content of 12.6 percent, this means a sensitivity of 0.2027 mg/l per chart unit as nitrocellulose. The detectability limit, normally taken as 2 chart units, is thus about 0.4 mg/l of nitrocellulose. The yield of nitrite ion was 70 percent of the stoichiometric amount for NC of 12.6 percent nitrate nitrogen content.

Analysis of Nitrocellulose through Determination of the Sum of Nitrite and Nitrate Ion Concentration Produced by Basic Hydrolysis. The complete automated hydrolysis sequence was used for this determination. The results, shown in Table 8, indicate a sensitivity of 0.083 mg/l as N per net chart unit. This seemingly excessive value will be discussed below.

Effect of the Presence of Glyceryl Trinitrate on Analysis of Nitrocellulose. Because glyceryl trinitrate is contained in many NC-based propellants and could be present in water emanating from NC-recovery operations, the effect of the compound on NC determination was investigated. Glyceryl trinitrate solutions, in concentrations of from 0.3 to 6 mg/l, were analyzed by the nitrite procedure both in the absence and presence of nitrocellulose. The dialyzer apparently removed a portion of the glyceryl trinitrate, but some came through in a manner suggesting continual adsorption and desorption. By itself, the glyceryl trinitrate produced discernible but skewed peaks, lower than for comparable concentrations (i.e., on the basis of nitrate ester content) of NC. The solvent (water) blanks that alternated with samples showed drift above the baseline, and the colorimeter readouts at the low points between samples and solvent blanks never returned to the baseline. This is uncharacteristic of the tracings for analysis of NC in the absence of glyceryl trinitrate. The glyceryl trinitrate interference was not alleviated by use of polytetrafluoroethylene ("teflon") tubing, increased wash to sample ratio, or addition of ethanol to the wash solution. Even after 20 samples of uncontaminated NC alternating with 20 solvent blanks, i.e., 1 hour of operation, the glyceryl trinitrate signals were observable, though at successively lower levels.

22
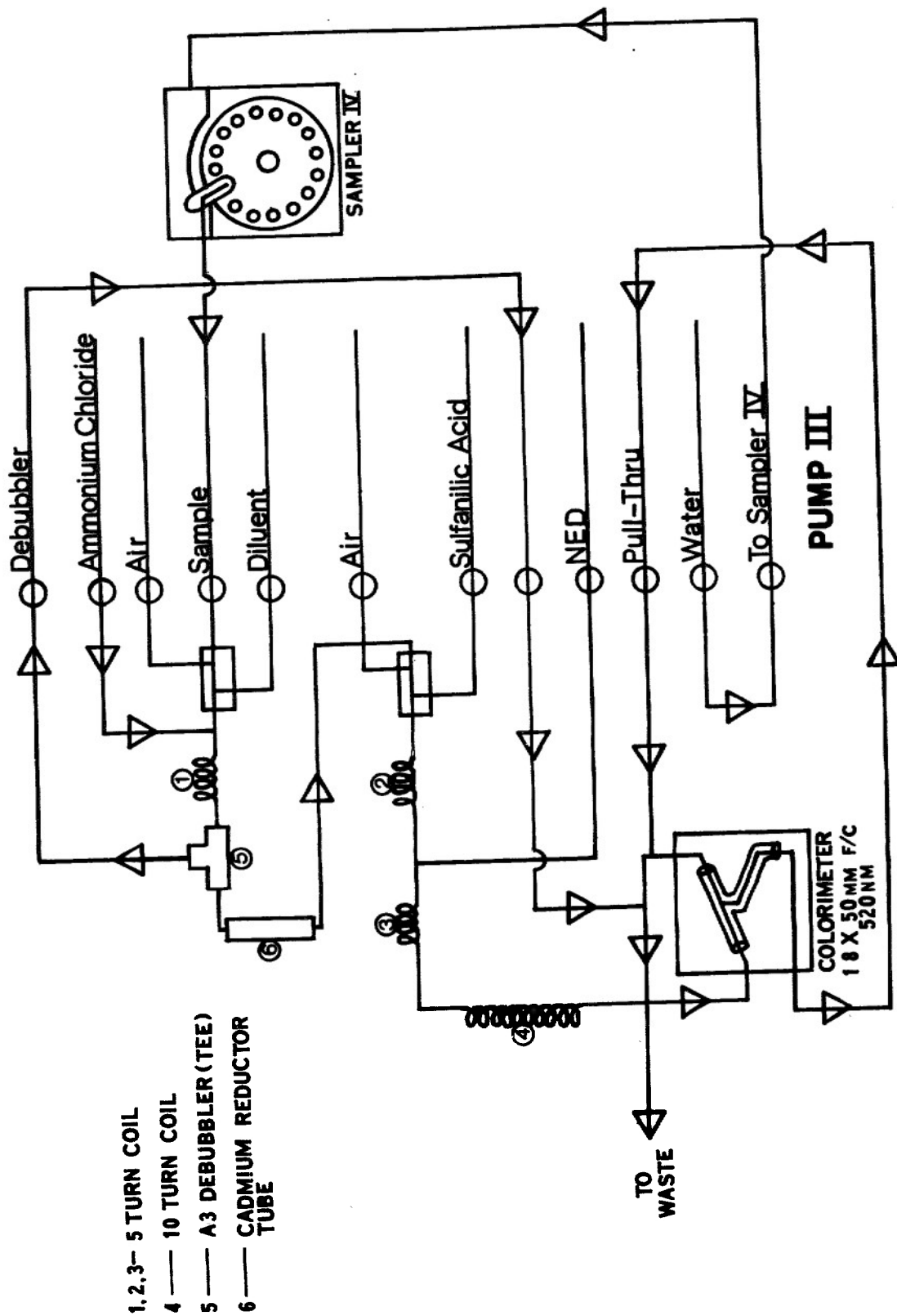
Figure 7. Technicon AutoAnalyzer Assembly for Nitrate Analysis.

1, 2, 3 — 5 TURN COIL
4 — 10 TURN COIL
5 — A3 DEBUBBLER (TEE)
6 — CADMIUM REDUCTOR TUBE

SAMPLER IV

Debubbler
Ammonium Chloride
Air
Sample
Diluent
Air
Sulfanilic Acid
NED
Pull-Thru
Water
To Sampler IV

PUMP III

COLORIMETER
18 X 50 MM F/C
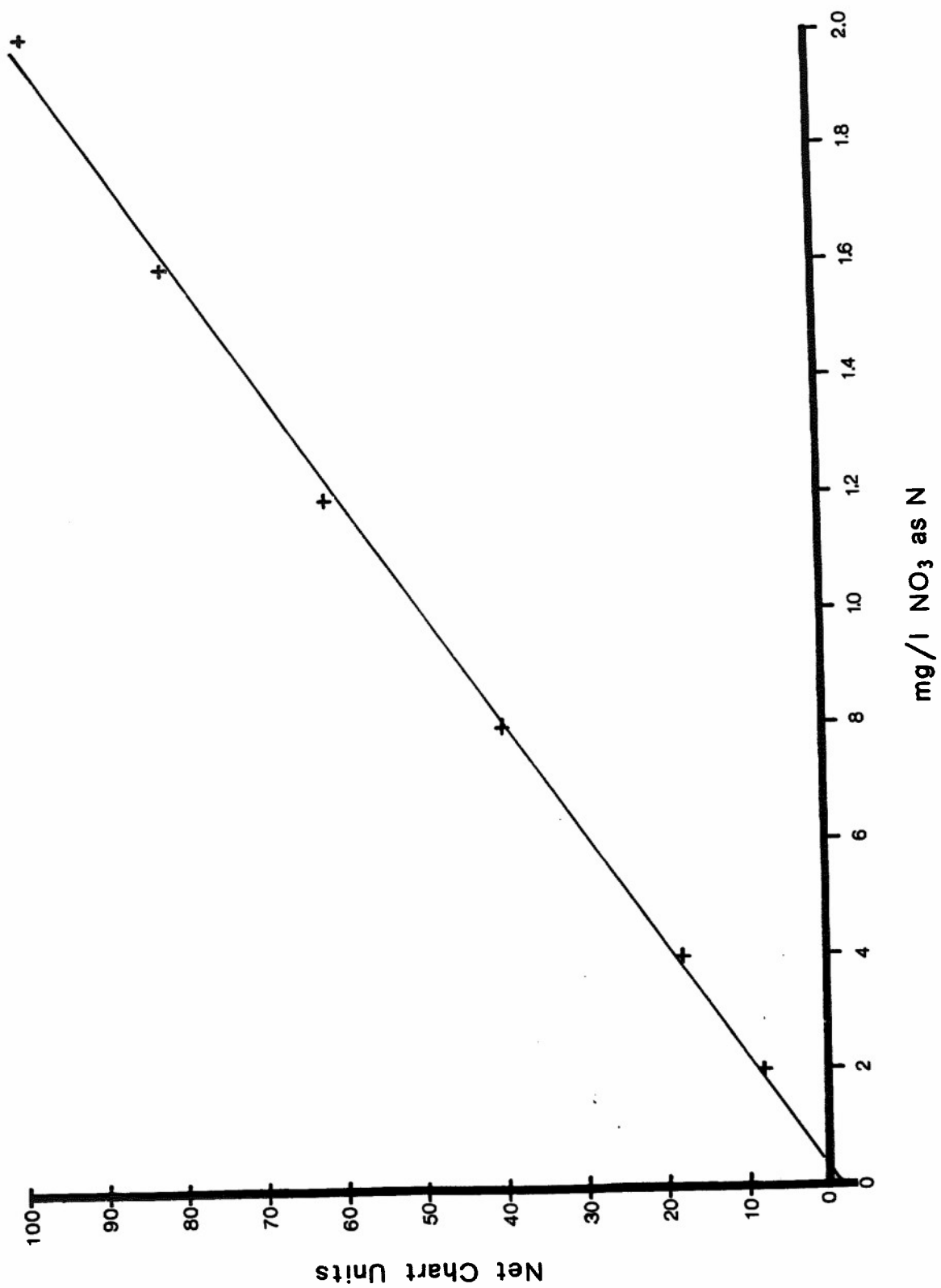520 NM

TO WASTE

23

Figure 8. Data Plot for Automated Nitrate Analyses.

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TABLE 6. RESULTS OF AUTOMATED ANALYSIS OF NITROCELLULOSE THROUGH
DETERMINATION OF CONCENTRATION OF NITRITE ION PRODUCED BY
BASIC HYDROLYSIS (RESULTS IN NET COLORIMETER UNITS, NCU)

Concentration, mg/l (as N)	Analysis Set Number				
	$I^{a,b}$ NCU	$II^{a,c}$ NCU	$III^{d,e}$ NCU	$IV^{d,f}$ NCU	$IV^{d,f}$ NCU
0.069	--	--	2.5	2.4	1.3
0.113	5.5	--	--	--	--
0.138	--	--	5.3	5.2	3.9
0.227	12.5	--	--	--	--
0.275	--	--	11.5	10.5	8.1
0.290	--	12.0	--	--	--
0.454	26.5	--	--	--	--
0.551	--	--	24.0	21.5	18.0
0.567	--	23.0	--	--	--
0.680	36.0	--	--	--	--
0.826	--	--	36.2	31.1	25.2
0.907	55.5	--	--	--	--
1.101	--	--	48.3	41.5	35.3
1.134	69.5	44.5	--	--	--
1.361	86.0	--	--	--	--
1.377	--	--	59.5	56.7	44.5
1.701	--	65.5	--	--	--
2.065	--	--	90.7	80.5	68.9

a. Calibration potentiometer set at 105.
b. 12 July 1973.
c. 25 July 1973.
d. Calibration potentiometer set at 060.
e. 11 November 1975.
f. 12 November 1975.

TABLE 7. SUMMARY OF DATA FROM AUTOMATED ANALYSIS OF NITROCELLULOSE
THROUGH DETERMINATION OF NITRITE ION PRODUCED BY BASIC HYDROLYSIS[a]

| Set Number | Calibration Factor [(Micrograms/liter) ÷ NCU] | | | |
	Mean	Standard Deviation	Range	95% Confidence Interval
I	17.60	1.69	4.71	1.56
II	25.07	0.81	1.80	1.29
III	24.01	1.82	4.83	1.52
IV	26.27	1.26	4.46	1.05
V	34.74	7.64	23.11	6.39
Mean	25.54[b]	6.14	17.14	7.62

a. See Table 6.
b. Mean of means.

TABLE 8. RESULTS OF AUTOMATED ANALYSIS OF NITROCELLULOSE
THROUGH DETERMINATION OF NITRATE PLUS NITRITE IONS
BY BASIC HYDROLYSIS (RESULTS IN NET COLORIMETER UNITS, NCU)[a]

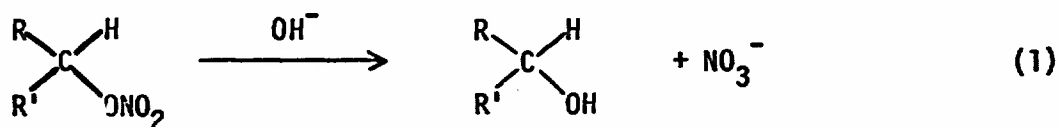| Concentration, mg/l (as N)	Triplicate Analyses NCU	Average NCU	Standard Error
0.22	2.5, 2.6, 2.4	2.5	0.06
0.44	5.2, 5.8, 5.2	5.4	0.20
0.88	11.8, 10.9, 10.8	11.2	0.32
1.76	21.9, 22.8, 21.3	22.0	0.44
2.64	30.1, 33.3, 31.7	31.7	0.92
3.52	43.5, 45.2, 40.6	43.1	1.34
4.40	62.6, 59.6, 57.8	59.9	1.28
7.04	83.1, 79.7, 83.5	82.1	1.21

a. Calibration factor [micrograms/liter ÷ NCU] = 83.

Determination of NC in Partially Treated Domestic Wastewater. At Badger Army Ammunition Plant, during its period of operation, non-industrial wastewater was combined with NC-containing discharges. For this reason, it was desirable to examine the effect of non-industrial wastewater on NC determination. The six wastewater samples (see *Reagents*) were analyzed in the automated analysis system for nitrite ion (as N), then spiked with NC and reanalyzed (without dialysis). Dialysis was then employed to remove the nitrite interference from the spiked samples. Results, shown in Table 9, indicate that the constituents of non-industrial wastewaters, including nitrite ion, do not interfere significantly with NC analysis when dialysis is employed.

DISCUSSION

Reaction Mechanisms

The alkaline denitrification of nitrate esters can occur through at least three pathways:[12]

$$\underset{\substack{R' \\ }}{\overset{R}{\underset{}{>}}} \underset{ONO_2}{\overset{H}{C}} \xrightarrow{\ OH^- \ } \underset{\substack{R' \\ }}{\overset{R}{\underset{}{>}}} \underset{OH}{\overset{H}{C}} \quad + \ NO_3^- \qquad (1)$$

Alcohol Production

$$\underset{\substack{R' \\ }}{\overset{R}{\underset{}{>}}} \underset{ONO_2}{\overset{H}{C}} \xrightarrow{\ OH^- \ } \underset{\substack{R' \\ }}{\overset{R}{\underset{}{>}}} C = 0 \quad + \ NO_2^- \qquad (2)$$

Carbonyl Production

$$\underset{\substack{R'' \\ }}{\overset{R}{\underset{}{>}}} C \underset{ONO_2}{\overset{H}{}} \xrightarrow{\ OH^- \ } \underset{\substack{R' \quad R'' \\ }}{\overset{R \quad H}{}} C = C \quad + \ NO_3^- \qquad (3)$$
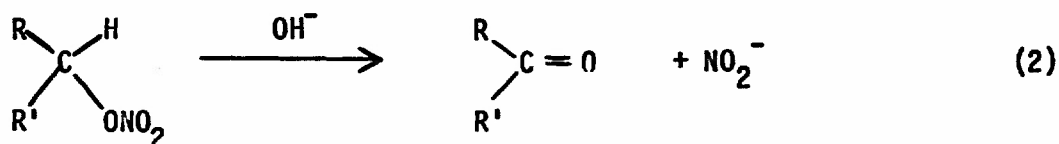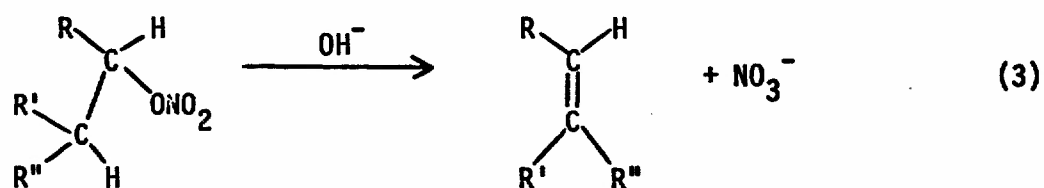
Olefin Production

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TABLE 9. RESULTS OF AUTOMATED ANALYSES FOR NITRITE AND NITROCELLULOSE IN TREATED DOMESTIC WASTEWATERS[a]

Sample No.	$[NO_2^-]$ as N, Sewage	$[NC]$ Added[b]	Expected $[NO_2^-]$ as N, Sewage + NC	Found $[NO_2^-]$ as N, Sewage + NC	$[NC]$ by Difference[c]	NC Recovery,[d] %
1	0.256	1.134	1.390	1.282	1.026	90.5
2	2.076	0.800	2.876	2.851	0.775	96.9
3	0.119	1.134	1.253	1.206	1.087	95.9
4	0.104	1.134	1.238	1.176	1.074	94.7
5	0.092	1.134	1.226	1.188	1.096	96.6
6	0.092	0.200	0.200	0.289	0.197	98.5

a. All concentrations in mg/l.
b. NC added as dry solid to 1 liter sewage sample.
c. ([NC] + Sewage) - Sewage.
d. ([NC] by difference/[NC] added) x 100.

According to Honeyman and Morgan,[13] the nitrate esters of sugars [and by extension, one would include nitrate esters of such carbohydrates as cellulose] react chiefly by pathway (2), an alpha-hydrogen elimination. This is followed by further degradation of the carbonyl compounds initially produced. In fact, the products of attack of hydroxide ion on NC have been found to include, in addition to nitrate and nitrite ions, also ammonia, carbon dioxide, sugars, organic acids (oxalic, malic, glycolic, trioxyglutaric, dioxybutyric, malonic and tartronic), and modified celluloses (e.g., nitrate esters).[14] As one might expect, the reaction rate for NC disappearance increases with temperature and hydroxide ion activity.[14] Nitrocellulose hydrolysis is also acid-catalyzed.[15] A minimum for susceptibility to hydrolysis at 37.8° is found[15] at pH 6.4, where the rate constant is 6.4×10^{-9} M hr^{-1}. NC is also decomposed by ultraviolet radiation.[16] NC decomposes thermally, igniting at 205°C.[17]

Choice of Conditions and Reagents

Because nitrocellulose is composed of rather dense small particles that tend to settle out, sampling is always a problem. In the automated procedure, both transfer of the sample to the sampling cups and withdrawal of samples from the cups into the AutoAnalyzer are subject to errors arising for sample heterogeneity. In the automated method, the sampling cup contents are stirred with a vibrator, and this is of considerable value, but the variations are still greater than those accompanying the analysis of true solutions.

The dialysis procedure was brought to a high level of efficiency by the use of sufficient membrane contact, a recipient stream of high enough salt concentration (which also slightly decreased the volume of the sample) and the countercurrent flow of that recipient stream. Thus, the presence of usual concentrations of nitrite, and presumably nitrate, in the original wastewater should not interfere with the analysis.

For the present automated (though not manual) study, the combination of 10 minutes at 70°C and 5 N sodium hydroxide sufficed to produce a useful yield of nitrite ion from NC. No attempt was made to determine if other combinations of temperature, time and caustic concentration would be equally effective or produce higher yields of nitrite ion.

The employment of the diazotization reaction (step 2 of the manual procedure) for nitrite determination is well known. Of the two amines recommended by Rider and Mellon,[18] sulfanilic acid was chosen (over sulfanilamide) because its acidity would assist in neutralizing excess alkali introduced in the first step.

On the recommendation of various investigators,[19-21] N-(1-naphthyl)-ethylenediamine (NED) was chosen as a faster and more efficient coupling agent (for step 3 of the manual procedure) than its chief competitor,

1-naphthylamine. A second justification is the fact that 1-naphthylamine is suspected as a human carcinogen.[22] Although chloramines, free chlorine and certain metal ions are known to interfere with such nitrite determinations,[11] their presence at significant levels in nitrocellulose-containing waste streams is unlikely.

Cadmium reduction of nitrate to nitrite, and determination of this nitrite along with that already present, was considered as the least complex means of analyzing a major portion of the NC nitrate ester functionality. In theory, it had the advantage of avoiding the consequence of variation in the nitrate/nitrite ratio. Though the choice was probably the best available, it still suffered from excessive susceptibility to variations in pH, even with the use of ammonium chloride as a buffer. This is one of the considerations leading to the recommendation (see below) to eliminate the nitrate reduction step.

Selection of a Procedure

It was necessary to carry out a number of experiments to determine the tradeoffs inherent in various choices of unit processes. Thus, the following insights were gained:

(1) The manual method, although simpler than the automated procedure, is subject to variation arising from the inability to reproduce the time-temperature cycle as well as can be done in the automated system. This may be reflected (not proved) in variable nitrate/nitrite ratios and yields.

(2) In the automated method, it is possible to incorporate a dialysis step to remove nitrite ion and nitrate ion. One or both of these ions (depending on the procedure used) would otherwise interfere with the analysis.

(3) The inclusion of several dialysis units increases the degree of nitrite (and nitrate) ion removal, but also increases the time requirements. Since there does not appear to be a real-time, or near real-time, analytical requirement, a 1-hour analysis time is acceptable.

(4) As would be expected from the theory of osmosis, a high saline content in the dialysis recipient stream (countersolution) is of advantage and involves no tradeoff.

(5) Countercurrent flow of the recipient stream is unusual, but increases the efficiency of nitrite removal; it involves no tradeoff. The introduction of fresh countersolution into each dialysis unit slightly complicates the experimental setup.

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(6) The colorimeter response was less for the nitrate/nitrite analysis than for nitrite analysis alone. This is attributable to peak broadening as a result of the cadmium reductor stage. Different results might be obtained if peak area integration, rather than measurement of the peak height, were used in the colorimetry step. Peak broadening would, however, increase the error of the method.

(7) Whereas nitrite ion interference is almost completely circumvented by the use of dialysis, interference by glyceryl trinitrate cannot be avoided by this stratagem. Glyceryl trinitrate is evidently adsorbed on the dialysis membrane and slowly moved into the basic hydrolysis region. The result of this is a gradually increasing baseline (i.e., increase in the reagent blank), as well as a contribution to the NC peak. This interference could not be circumvented during the time available for the study. Glyceryl trinitrate would be of concern only in wastewaters arising from recovery of NC from obsolete propellants.

(8) The constituents of non-industrial sewage do not interfere significantly with the automated nitrite method for nitrocellulose. In all probability, nitrite occurring in the industrial waste of NC manufacture would be removed satisfactorily by dialysis.

Based on the foregoing considerations, the automated approach minus step 3 (cadmium reduction) was selected as the analytical method of choice, with the use of four AAI dialyzer units (880 cm travel through the dialyzers) to remove nitrite interference. The configuration of choice is shown in Figure 9.

CONCLUSION

An automated procedure, using a Technicon AutoAnalyzer in the configuration of Figure 9, has been developed for the analysis of nitrocellulose suspensions in wastewaters. The limit of detectability is about 0.4 mg/l of nitrocellulose. This limit is well below the 1983 Best Available Technology Effluent Limitation of 10 mg/l for total suspended solids, which is most likely to govern the discharge of nitrocellulose. Instrumental adjustments could be made to decrease the sensitivity of the method, but increase reproducibility, in the range of 2-10 mg/l. It is recognized that the user would have to make a final evaluation, and possibly adjustments in the procedures, at the time the automated procedure is introduced. Glyceryl trinitrate, if present, could be a serious interference. Non-industrial wastewater, containing nitrite ion, did not interfere significantly with the analyses.
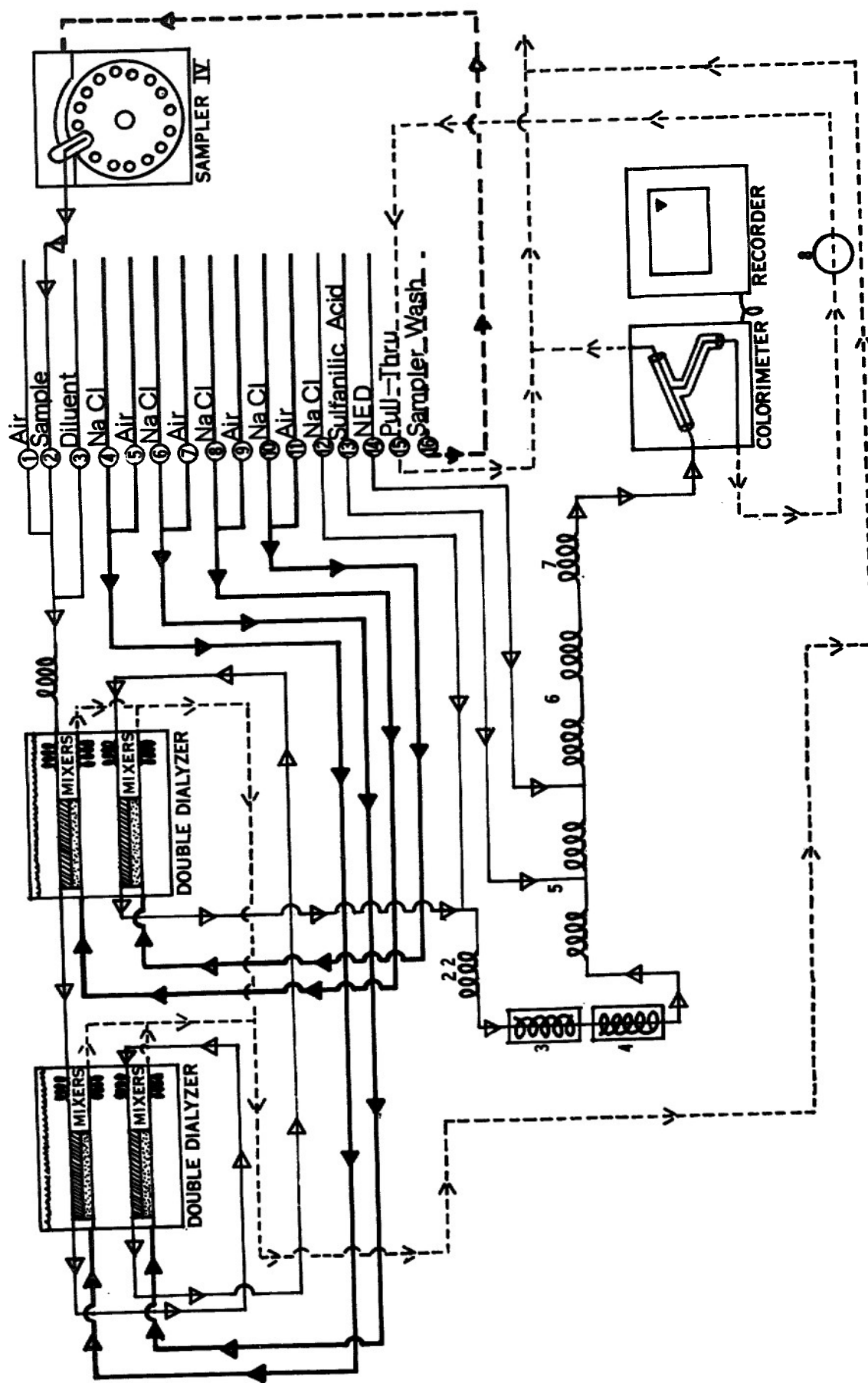
31

Figure 9. Recommended Technicon AutoAnalyzer Assembly for Automated Analysis of Nitrocellulose in Wastewaters Containing Nitrite Ion.

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